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(54) Title: COMPATIBILIZED LCP BLENDS (57) Abstract <p>The present invention provides alloys having at least one thermotropic liquid crystalline polymer, at least one thermoplastic aromatic polyester and at least one compatibilizer and methods of making such alloys.</p>		

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COMPATIBILIZED LCP BLENDS

5 **FIELD OF THE INVENTION**

The present invention provides alloys comprising thermotropic liquid crystalline polymers (LCPs) and at least one thermoplastic aromatic polyester and at least one compatibilizer.

10 **BACKGROUND**

High performance plastics are in widespread use in many industries and there is much interest in developing new plastics which are economical and recyclable, as well as high performance. The blending and alloying of existing polymers is a cost effective way to produce new high performance plastics which meet these criteria.

Polymer blends containing thermotropic LCPs have received increasing attention in the scientific and technical literature. The range of high performance thermoplastic flexible polymers which have been blended with TLCPs include polyimides, polyamides, poly(ethersulfone) (PES),
20 poly(etherimide) (PEI), polyetherketone (PEEK), polycarbonate (PC),
poly(ethylene terephthalate) (PET), poly(ethylene naphthalate) (PEN),
polyphenylene sulfide (PPS), and polyarylate.

Thermotropic LCPs are a relatively new class of high performance polymeric materials which combine the advantages of melt processability
25 and outstanding mechanical properties. Because of their rigid backbone
structure with flexible spacer groups, commercially available thermotropic LCPs have far higher tensile strength and flexural moduli than conventional polymers. However, thermotropic LCPs are in many cases difficult to process without specialized equipment and very costly as compared with
30 conventional polymers when used alone.

Blending thermotropic LCPs with other polymers has been shown to improve processability of the other polymers, particularly LCPs based on wholly aromatic chain segments. Furthermore, blending with conventional thermoplastic polymers reduces costs, because less of the very costly LCP is

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used. Also, because thermotropic LCPs form an ordered phase in the melt (hence, the name thermotropic), they have shear viscosities far lower than other polymers and thus, have potential importance as a processing aid in mixtures with other polymers by reducing the melt viscosity of the mixture.

5 Thermotropic LCP in blends with polyethylene terephthalate (PET), have been reported to act as a "flow aid" at levels of 5-10% by reducing the melt viscosity. In U.S. Patent Nos. 4,386,174, 4,433,083, and 4,438,236, it is disclosed that blending a thermotropic LCP with other polymers such as PET changes the melt viscosity of PET. At 10% loading (LCP) the
10 viscosity of PET is reduced to 25-50% of its original viscosity. O'Brien and Crosby (O'Brien, G.S. and Crosby, J.M., Proceedings of COMPALLOY '91 Conference, January 30-February 1, 1991, pp. 133-148) described LCP/PTFE blends to improve the flow of PTFE in the melt.

The use of thermotropic LCPs in blends to provide "reinforcement,"
15 especially where the LCP has a very rigid structure has been reported. XYDAR® (Poly(oxybenzoyl-co-bisphenyl terephthalate), Amoco, and VECTRA® Poly(oxybenzoyl-co-oxynaphthoyl), Hoechst-Celanese, are thermotropic LCPs which have been much studied as blend components. Crevecoeur, G. and Groeninckx, G., *Polymer Eng. Science*, 30, 532
20 (1990), reported that a thermotropic LCP can be used at 5-30% levels in polystyrene so that the LCP forms a disperse phase. In a 75:25 Polystyrene/VECTRA® A-950 LCP blend at a draw ratio of 5, the LCP phase was reported as being slightly elongated. However at a draw ratio of 10 or more, the LCP phase was reported to show a well-developed micro-
25 fibrillar morphology and to display a substantial increase in elastic modulus over a compression or injection-molded sample.

The use of LCPs in blends with thermoplastic polymers, e.g., PC and PAT, to achieve improved mechanical properties over those of the

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thermoplastic polymer alone was reported in 1989. See, Bonis, L.J., "Multilayer Thermoplastics Advance Composites By Coextrusion", *The Polymer Processing Society Summer Meeting*, Amherst, Massachusetts, August 16-17, 1989, Paper 10F. See, also Williams, D.J., Proceedings of COMPALLOY '91 Conference, January 30 - February 1, 1991, pp. 393-408 which describes potential applications for thermotropic liquid crystal polyester blends.

Polymer molding compositions containing polycarbonates, thermoplastic polyester, and liquid crystalline polymers, wherein the liquid crystalline polymer is present as droplets or low aspect ratio particles, are disclosed in U.S. Patent No. 5,262,473. In the process disclosed in U.S. Patent No. 5,262,473, compatible blends of the polyester and polycarbonate may be used. Other blends are disclosed in, for example, U.S. Patent Nos. 5,070,157 and 5,156,785.

A blend is a physical mixture of two or more components which typically offers a compromise of properties and economies of the individual components. It is well known that the nature and properties of the interface of components in a blend frequently exert a limiting effect on the bulk properties of a multi-phase blend material. In fact, the physical and mechanical properties of a blend are very often inferior to the mathematical average of the properties of the original components. Blend components can be miscible or immiscible in their behavior toward each other.

Alloys are different from blends. Although they are also composed of two or more components, alloys exhibit strong intermolecular forces wherein intermolecular bonding between the components of the blend is provided by compatibilizers. This bonding in turn, creates new properties different from those of the original components and often exceeding those of the average of the original ingredients. The types of interaction or

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"chemical bonding" between the components can include, for example, one or more of the following mechanisms: ionic; covalent; molecular inter-penetration; hydrogen bonding; or associative.

5 Successful compatibilization by one or more of these interactions gives rise to interfacial adhesion to provide the formation of cohesive multi-phase compatibilized alloys with useful properties. To achieve compatibilization a number of strategies have emerged.

10 In one approach, suitable block or graft copolymers are introduced to serve as macromolecular emulsifiers providing covalent bonds that traverse and fortify the blend interface. Block and graft copolymers may be generated *in-situ* through reactive extrusion and blending to generate a compatibilized blend.

15 In another approach, polymers having nucleophilic functional groups are interacted with compatibilizers containing hydrogen to form hydrogen bonding. Ionomers have also served as compatibilizers. In some cases, ionic or strong physicochemical interactions are generated across the interface, which in turn enhances compatibilization.

20 Compatibilization can also result from the addition of a similar functional group using the "like attract like" theory, such as the use of chlorinated polyethylene to compatibilizer polyvinyl chloride with polyethylene. This has been referred to as "associative" bonding.

25 Finally, compatibilization has even been demonstrated by the addition of a third immiscible phase component that exhibits relatively low interfacial tension with each of the primary blend components, i.e., those components intended to be compatibilized. The compatibilizing effects of the mutually miscible component may result from its presumed tendency to become enriched in the vicinity of the blend interface.

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Alloying provides a tool to lower the cost of high performance resins while at the same time retaining many of the desirable properties and/or providing improved properties such as increased processability. The most successful alloying procedures result in a controlled and stable morphology with a singular thermodynamic profile. However, even when alloying is not "complete" in the multi-component system useful compositions can result.

At present, there is no known direct compatibility between LCPs and thermoplastic aromatic polyesters.

Accordingly, approaches to compatibilize LCPs with thermoplastic aromatic polyesters and, thereby, to provide LCP/thermoplastic aromatic polyester alloys having properties which can be tailored to meet end-use specifications are being sought.

SUMMARY OF THE INVENTION

The present invention provides alloys comprising at least one thermotropic LCP, at least one thermoplastic aromatic polyester, and at least one compatibilizer. In one preferred embodiment, two compatibilizers are present.

Preferred compatibilizers include:

- (1) copolyester elastomers;
- (2) ethylene ester copolymers, such as ethylene-methyl acrylate copolymers;
- (3) copolymers of ethylene and a carboxylic acid or acid derivative, such as ethylene-maleic anhydride copolymers;
- (4) ethylene ester copolymers, such as ethylene methyl acrylate copolymers, grafted with functional monomers;
- (5) ethylene copolymer-acrylic acid terpolymers, such as ethylene-methyl acrylate-maleic anhydride terpolymers;

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(6) terpolymers of ethylene, unsaturated ester and a carboxylic acid or acid derivative, such as ethylene-methyl acrylate-methacrylic acid terpolymers; and

(7) acrylic elastomers, such as acrylic rubbers.

5

Copolymers and terpolymers comprising ethylene-methyl acrylate, copolyester elastomers and acrylic elastomers are particularly preferred compatibilizers for use in the present invention.

A particularly preferred:

10

(i) copolyester elastomer is HYTREL™ HTR-6108 from DuPont;

(ii) ethylene-methyl acrylate copolymer is SP 2205™ and 3306™ from Chevron Chemical Company;

15

(iii) ethylene maleic anhydride copolymer is Polybond™ 3009 from BP Chemicals and Fusabond® E-MB-226D from DuPont Canada;

20

(iv) ethylene-methyl acrylate copolymer grafted with maleic anhydride is DS™ 1328/60 from Chevron Chemical Company and Fusabond® A MG-175D from DuPont Canada;

(v) ethylene-methyl acrylate-maleic anhydride terpolymer is Lotader™ 2400, Lotader™ 3410, and Lotader™ 5500 from Elf Atochem;

25

(vi) ethylene-methyl acrylate-methacrylic acid terpolymer is Escor® ATX-320, Escor® ATX-325 or Escor® XV-1104 from Exxon Chemical; and

(vii) acrylic rubber is Vamac™ G1 from DuPont.

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Thermoplastic aromatic polyesters for use in the present invention are commonly referred to by those skilled in the art as PET polymers and include but are not limited to PET (homopolymers and copolymers), polybutylene terephthalate (PBT), PETG (PET modified with cyclohexanedimethanol (CHDM)), PCTA copolymers (a polymer of CHDM and terephthalic acid with another acid substituted for a portion of the terephthalic acid), PBT (polybutylene terephthalate), APET (amorphous polyethylene), CPET (cystallizable PET), PCPT (copolyester containing propylene glycol), PEN (polyethylene naphthalate), and PBN (polybutylene naphthalate). Preferred thermoplastic aromatic polyesters include PET homopolymers and copolymers containing terephthalic acid and isoterephthalic acid, and PCTA. Especially preferred thermoplastic aromatic polyesters include Eastman Kodak Company's Kodar® or Eastar® A150, Kodar® or Eastar™ 9921, Kodapak® or Eastapak™ 7352, Kodar® or Eastar™ 9921W and Eastman™ 1339; Shell's Traytuff™ 8006; DuPont's Crystar™ 1927 and Selar™ PT7067; and Shell's Traytuff™ CPET.

Preferred thermotropic LCPs include wholly or partially aromatic polyesters or copolyesters. Particularly preferred copolyesters include XYDAR™, VECTRA™ and ZENITE™ (E.I. duPont de Nemours).

Other preferred thermotropic liquid crystal polymers include SUMIKASUPER® and EKONOL™ (Sumitomo Chemical), DuPont HX™, RODRUN® (Unitika) and GRANLAR™ (Grandmont).

Preferred LCPs for use in the present invention include any such resins with a melt temperature in the range of 250 to 350°C. Particularly preferred LCPs have a melt temperature in the range of 250 to 280°C.

One preferred alloy in accordance with the present invention comprises thermoplastic aromatic polyester, a wholly aromatic LCP copolyester and an ethylene-methyl acrylate-acrylic acid terpolymer

compatibilizer, for example, Escor® ATX-320, Escor® ATX-325, or Escor® XV-1104.

Another preferred alloy comprises thermoplastic aromatic polyester, a wholly aromatic LCP copolyester and a ethylene maleic anhydride copolymer compatibilizer such as Polybond™ 3009 or Fusabond® E-MB-226D.

Yet another preferred alloy in accordance with this invention comprises thermoplastic aromatic polyester, a wholly aromatic LCP copolyester and an ethylene-methyl acrylate copolymer grafted with maleic anhydride compatibilizer, such as DS™ 1328/60, or an ethylene acrylate terpolymer grafted with maleic anhydride such as Fusabond® A MG-175D, or a copolyester elastomer such as HYTREL™ HTR 6108.

Alloys comprising thermoplastic aromatic polyester, LCP and at least two compatibilizers are particularly preferred in the practice of the present invention. The compatibilizers are preferably selected from a copolyester elastomer, ethylene-maleic anhydride copolymer, ethylene-methyl acrylate copolymer, ethylene-methyl acrylate copolymer grafted with maleic anhydride, ethylene-methyl acrylate-maleic anhydride terpolymer, ethylene-methylacrylate-methacrylic acid terpolymer, or acrylic rubber.

Preferred two compatibilizer alloys include a PCTA copolymer such as Kodar® or Eastar™ A150, a wholly aromatic LCP copolyester, an ethylene-methyl acrylate-acrylic acid terpolymer and ethylene maleic anhydride copolymer compatibilizer. Exemplary ethylene-methyl acrylate-acrylic acid terpolymers include Escor® ATX-320, Escor® ATX-325, or Escor® XV-1104 and an exemplary ethylene maleic anhydride copolymers are Polybond™ 3009 and Fusabond® E-MB-226D.

In other preferred thermoplastic aromatic polyester/LCP alloys, the LCP comprises a wholly aromatic copolyester and the compatibilizers are a

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unsaturated ethylene ester copolymer grafted with maleic anhydride and/or an ethylene-maleic anhydride copolymer. Exemplary unsaturated ethylene ester copolymers grafted with maleic anhydride are the ethylene-methyl acrylate copolymers SP 2205™ and 3306™, and exemplary ethylene-maleic anhydride copolymers are Polybond™ 3009 and Fusabond® E-MB-226D.

Another preferred thermoplastic aromatic polyester/LCP alloy of the present invention comprises a wholly aromatic LCP copolyester and ethylene ester copolymer grafted with maleic anhydride and an ethylene-maleic anhydride copolymer compatibilizer.

Yet another preferred alloy comprises thermoplastic aromatic polyester, wholly aromatic LCP copolyester, and a copolyester elastomer such as HYTREL™ HTR 6108 and an ethylene maleic anhydride copolymer, such as Polybond™ 3009 and Fusabond® E-MB-226D.

The ethylene-methyl acrylate copolymers grafted with maleic anhydride, DS™ 1328/60 and Fusabond® A MG-175D, and the ethylene maleic anhydride copolymers, Polybond™ 3009 and Fusabond® E-MB-226D, are particularly preferred when the LCP is VECTRA™ A-950. Also preferred when the LCP is VECTRA™ A-950 are the compatibilizers Polybond™ 3009 or Fusabond® E-MB-226D and a second compatibilizer, Escor® ATX-320, Escor® ATX-325, DS™ 1328/60, Fusabond® A MG-175D, Escor® XV-1104, or HYTREL™ HTR-6108.

The properties of the LCP and thermoplastic aromatic polyester, as well as desired properties of the resulting alloy, are all taken into consideration in selecting suitable compatibilizers for use in the present invention. The properties of the thermoplastic aromatic polyester/LCP alloys of the present invention are adjusted by adjusting the amount of compatibilizer and, in some preferred embodiments, by the manner in which the components are combined.

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Because the most expensive component in the alloys of the present invention typically is the LCP, in order to reduce costs it is preferable to keep the LCP content of the composition as low as possible while achieving the desired effect. Hence, in the present alloys the LCPs are used as the
5 disperse phase, whereas thermoplastic aromatic polyester is used as the predominant or bulk phase.

When no compatibilization exists between thermoplastic aromatic polyester and LCP, such as when no compatibilizer is present, the mechanical properties of the resulting blend are low. For example, in films
10 extruded from blends comprising 10% LCP / 90% PCTA (Kodar® or Eastar™ A-150) a machine direction (MD) tensile strength of only about 6,000 psi and MD tensile modulus of only about 300,000 psi are obtained. Furthermore, the oxygen barrier properties are poor, for example, around
15 35 to 40 cc-mil/10in²-24 hours-1 atm. It was unexpectedly found that when thermoplastic aromatic polyester/LCP alloys were formed by adding suitable compatibilizers in accordance with the teachings of the present invention, improved mechanical properties and/or lower gas permeation (barrier) numbers were obtained.

The present invention also provides methods of preparing the alloys
20 described above. These methods include:

- i. LCP, thermoplastic aromatic polyester and at least one compatibilizer are mixed and melt blended to form an alloy;
- ii. LCP, thermoplastic aromatic polyester and a
25 portion of the total compatibilizer to be used are mixed and melt blended, the remainder of the compatibilizer is added at a later time and further melt blended;

- iii. LCP, thermoplastic aromatic polyester and a first compatibilizer are mixed and melt blended. A second compatibilizer is added to the melt blend at a later time and further melt blended;
- iv. LCP and thermoplastic aromatic polyester are mixed and melt blended and at least one compatibilizer is added at a later time to the melt blend and further melt blended;
- v. Thermoplastic aromatic polyester is melted under appropriate conditions in an extruder and at a later time LCP and at least one compatibilizer are added to the thermoplastic aromatic polyester and further melt blended;
- vi. Thermoplastic aromatic polyester and a first compatibilizer are melt blended and at a later time LCP and a second compatibilizer are added to the melt blend and further mixed and melt blended;
- vii. Thermoplastic aromatic polyester and LCP are mixed and melt blended and two compatibilizers are added to the melt blended and further melt blended; and
- viii. Thermoplastic aromatic polyester, LCP and two compatibilizers are mixed and simultaneously melt blended.

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DETAILED DESCRIPTION OF THE INVENTION

The LCP/thermoplastic aromatic polyester alloys of the present invention are formed by use of at least one compatibilizer. In one preferred embodiment, two compatibilizers are used to form the alloys.

5 The alloys of the present invention comprise from about 0.5 to about 10 weight percent thermotropic liquid crystalline polymer, from about 40 to about 90 weight percent thermoplastic aromatic polyester, and from about 1 to about 50 weight percent compatibilizer.

10 The liquid crystalline polymer is preferably present in amounts from about 5 to about 10 weight percent, thermoplastic aromatic polyester is preferably present in amounts from about 70 to about 93 weight percent and one or more compatibilizers are present in amounts from about 2 to about 20 weight percent.

15 In a particularly preferred embodiment, the compositions of the present invention contain from about 9 to about 12 weight percent LCP, from about 78 to about 86 weight percent thermoplastic aromatic polyester, and from about 5 to about 10 weight percent compatibilizer.

20 Thermoplastic aromatic polyesters suitable for use in the present invention are prepared by methods well known in the art. A variety of methods for making suitable PET homopolymers and copolymers are well known in the art. For example, one suitable PET for use in the present invention is prepared by the reaction of either terephthalic acid or dimethyl terephthalate with ethylene glycol. Various copolymers of PET have been developed and are also prepared by methods well known to the skilled
25 artisan. Suitable thermoplastic aromatic polyester is also available commercially from a number of vendors. Especially preferred commercially available thermoplastic aromatic polyesters include Eastman Kodak Company's Kodar® or Eastar® A150, Kodar® or Eastar™ 9921,

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Kodapak® or Eastapak™ 7352, Kodar® or Eastar™ 9921W and Eastman™ 1339; Shell's Traytuff™ 8006; DuPont's Crystar™ 1927 and Selar™ PT7067; and Shell's Traytuff™ CPET.

Suitable PCTA copolymers e.g., Kodar® or Eastar™ A150, for use in
5 the present invention are prepared by the reaction of terephthalic acid
isophthalic acid, and cyclohexane dimethanol. Kodar® or Eastar™ A150 is
one preferred commercially available PCTA for use in the present
invention. Preferred commercially available PETs include a PET
homopolymer produced from dimethyl terephthalate and ethylene glycol
10 such as Kodapak® or Eastapak™ 7352; a PET copolymer comprising
terephthalic acid, isoterephthalic acid and ethylene glycol such as Shell's
Traytuff™ 8006; and a CPET such as Shell's Traytuff™ CPET.

Suitable thermotropic LCPs for use in the present invention include
wholly and partially aromatic polyesters and co-polyesters such as those
15 disclosed in U.S. Patent Nos. 3,991,014, 4,067,852, 4,083,829, 4,130,545,
4,161,470, 4,318,842, and 4,468,364. Preferred thermotropic LCPs
include wholly or partially aromatic polyesters or copolyesters. Particularly
preferred copolyesters include XYDAR™, VECTRA™ and ZENITE™ (E.I.
duPont de Nemours). Other preferred thermotropic liquid crystal polymers
20 include SUMIKASUPER® and EKONOL™ (Sumitomo Chemical), DuPont
HX™, RODRUN® (Unitika) and GRANLAR™ (Grandmont).

Vectra™ A950, sold by Celanese Research Corporation, Summit,
New Jersey is one preferred wholly aromatic copolyester. This polymer has
been reported to consist essentially of about 25-27 percent of 6-oxy-2-
25 naphthoyl moieties and about 73-75 percent of p-oxybenzoyl moieties, as
described in example 4 of U.S. Patent No. 4,468,364 and in G. W.
Calundann et al., "Anisotropic Polymers, Their Synthesis and Properties",
reprinted from Proceedings of the Robert A. Welch Conferences on

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Chemical Research, XXVI Synthetic Polymers, November 15-17, 1982, Houston, Texas, pp. 247-291 (see especially pp. 263-265).

Another particularly preferred thermotropic LCP is ZENITE™. This polymer has been reported to consist of hydroxy-benzoic acid/phenyl
5 hydroquinone/dimethyl-napthylene dicarboxylate units.

In formulating the composition of the alloys of the present invention a number of variables including, the properties of the polymers to be blended, properties of the compatibilizers, and the amount and ratio of the components, are taken into consideration. These variables are tailored and
10 optimized in accordance with the present teachings to provide alloys to meet a particular end use specification. For example, if high gas barrier properties are desired, then polymers having high individual gas barrier properties are preferably selected.

The amount of compatibilizer is adjusted to provide intermolecular
15 bonding among the components of the alloy to enhance properties and at the same time, to avoid the formation of a quasi- or pseudo-cross linked network which is not readily processable.

The compatibilizers for use in the present invention are either miscible with each of the LCP and the thermoplastic aromatic polyester through, e.g., covalent, ionic, molecular inter-penetration, hydrogen
20 bonding or associative interactions as mentioned above, or have interactive miscibility when the LCP and thermoplastic aromatic polyester are present in a common phase. In other words, the functional groups of the compatibilizer, LCP, and thermoplastic aromatic polyester for use in the
25 alloys are also chemically compatible. For example, if the LCP to be alloyed with thermoplastic aromatic polyester has an aliphatic type of polyester functionality, such as acrylate or methacrylate, or an aromatic functionality, such as a benzoate or phthalate ester linkage, then preferred

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compatibilizers will have a functionality, such as a polyester functional group or a maleic anhydride functional group, that is capable of reacting with the polyester group.

Compatibilizers for use in the present invention are also processable in the melting and processing range of thermoplastic aromatic polyester and the LCP and exhibit temperature stability at the intended processing temperature. By temperature stability is meant that a component of the alloy essentially retains its chemical functionality and, hence, its interfacial interaction with the other components of the alloy with which it interacts. If one of the components were not thermally stable, it is possible that the compatibilization achieved could fail on subsequent processing.

Preferred alloys of the present invention comprise at least one thermotropic LCP, thermoplastic aromatic polyester, and at least one compatibilizer. Particularly preferred embodiments include two or more compatibilizers, wherein at least one compatibilizer interacts with the LCP and at least one interacts with the thermoplastic aromatic polyester. The ratios of compatibilizers to each other and in the total composition are adjusted to achieve alloys having the desired properties as is shown in the examples which follow.

The following compatibilizers are particularly preferred in the practice of the present invention wherein components of the alloy comprise thermoplastic aromatic polyesters and wholly aromatic esters and copolyesters liquid crystal polymers, such as VECTRA™ and XYDAR™:

- i. Copolyester elastomers such as HYTREL™
HTR-6108 from DuPont;
- ii. Ethylene maleic anhydride copolymers
including HDPE grafted with maleic anhydride,
such as Polybond™ 3009 from BP Chemicals,

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and a linear low density polyethylene-maleic anhydride graft such as Fusabond® E-MB-226D from DuPont of Canada;

- 5 iii. Ethylene-methyl acrylate copolymers, such as
SP 2205™ and SP3306™ from Chevron
Chemical Company;
- iv. Ethylene-methyl acrylate copolymers grafted
with maleic anhydride, such as DS™ 1328/60
10 from Chevron Chemical Company and
Fusabond® A MG-175D from DuPont Canada;
- v. Ethylene-methyl acrylate copolymer, such as
Lotader™ 2400, Lotader™ 3410 and Lotader™
5500 from Elf Atochem;
- 15 vi. Ethylene-methyl-methacrylic acid terpolymers
(ethylene-methyl acrylate-acrylic acid
terpolymers) such as Escor® ATX-320, Escor®
ATX-325, and Escor® XV-1104 from Exxon
Chemical; and
- 20 vii. Acrylic rubber such as VAMAC™ G1 from
DuPont.

 The alloys of the present invention can be extruded to form various articles of manufacture such as films and tubes useful, e.g., in food packaging, electronic circuit substrates and structural applications. The
25 films can be thermoformed to provide, e.g., trays, blow molded to, e.g., form containers, and otherwise processed by known methods. In some embodiments, articles of manufacture comprising the alloys of the present invention are provided with a thin coating of, e.g., glass, metal or another

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polymer both to protect the article and to provide suitable means to affix labels and the like.

To illustrate the improved properties of the alloys of the present invention, various alloys were prepared as taught herein and extruded to form films having improved tensile strength, tensile modulus and/or oxygen barrier properties over films extruded from thermoplastic aromatic polyester or LCP and thermoplastic aromatic polyester blends without compatibilizers. In some films, tensile strength was increased by up to more than 2 times and tensile modulus was increased up to more than 3 times over that of the blend without compatibilizer. In many instances, values above 10,000 psi and tensile strength and/or above 500,000 psi and tensile modulus were obtained.

Films extruded from alloys comprising thermoplastic aromatic polyesters including PCTA and PET homopolymers, a wholly aromatic copolyester LCP, and a compatibilizer selected from a copolyester elastomer; a copolyester elastomer and an ethylene ester copolymer grafted with maleic anhydride; or an ethylene-methyl acrylate-methacrylic acid terpolymer.

Films extruded from alloys comprising thermoplastic aromatic polyester, and an anhydride-grafted ethylene-methyl acrylate copolymer, thermotropic LCP wholly aromatic copolyester and a ethylene ester copolymer grafted with maleic anhydride showed improved mechanical properties.

Films extruded from three component alloys comprising thermoplastic aromatic polyester, wholly aromatic copolyester and an ethylene-methyl-methacrylic acid terpolymer, e.g., Escor® ATX-320 or -325, had superior mechanical properties. Also, three component blends comprising thermoplastic aromatic polyester, wholly aromatic copolyester

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and a copolyester elastomer such as HYTREL™ HTR-6108 were extruded to produce films having superior mechanical properties.

A number of films extruded from the alloys of the present invention yielded low oxygen permeation values, ranging from about 18 to 30, well
5 below the 36 to 40 cc-mil/10in²-24 hours-1 atm expected for Kodar® or Eastar™ A150 and in another case ranging from about 8 to 22, well below the about 28 cc-mil/10in²-24 hours-1atm expected for Kodapak® or Eastapak™ 7352.

Films extruded from alloys comprising PCTA such as Kodar® or
10 Eastar™ A150, a wholly aromatic copolyester LCP and a copolyester elastomer such as HYTREL™ HTR-6108 had excellent barrier properties. Also, films extruded from alloys comprising thermoplastic aromatic polyester, a copolyester elastomer, such as HYTREL™ HTR-6108, a wholly aromatic copolyester, and ethylene maleic anhydride copolymer, such as
15 Polybond™ 3009, had excellent oxygen barrier properties, e.g., from about 21 to 23 cc-mil/10in²-24 hours-1 atm. Excellent barrier properties were also obtained with films extruded from alloys comprising Kodapak® or Estapak™ 7352, VECTRA™ A-950 and Escor® ATX-325 or HYTREL™ HTR-6108. One preferred alloy comprised Kodapak® or Estapak™ 7352 at
20 about 87%, HYTREL™ HTR-6108 at about 3%, and VECTRA™ A-950 at about 10%. Another preferred alloy comprised Kodapak® or Estapak™ 7352 at between about 88-89%, Escor® ATX-325 at about 2 to 4%, and VECTRA™ A-950 at 10%. See Table Q. The over 3 times improvement in barrier equal to over 3 times reduction in permeability was unexpected.

25 The optimum amount of compatibilizer to obtain the desired reduction in permeability will vary depending upon run conditions but such optimum amounts are readily determined by the skilled artisan in view of the present teachings.

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Optional components well known to the skilled artisan may be added to alloys of the present invention provided that they do not interfere with formation or with the desired final properties of an alloy. Such additives includes fillers and pigments, lubricants, mold release agents, plasticizers, ultraviolet stabilizers and so forth.

In the methods of the present invention, compatibilizers are used either alone or in various combinations with LCP and thermoplastic aromatic polyester to achieve the desired results. They are also used in single step and sequential compatibilization methods as described below.

The following methods have been found to provide alloys having improved properties which can be used, e.g., to provide films having improved properties over films of LCP and thermoplastic aromatic polyester blends. These methods include:

- i. LCP, thermoplastic aromatic polyester and at least one compatibilizer are mixed and melt blended to form an alloy;
- ii. LCP, thermoplastic aromatic polyester and a portion of the total compatibilizer to be used are mixed and melt blended, the remainder of the compatibilizer is added at a later time and further melt blended;
- iii. LCP, thermoplastic aromatic polyester and a first compatibilizer are mixed and melt blended. A second compatibilizer is added to the melt blend at a later time and further melt blended;

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- iv. LCP and thermoplastic aromatic polyester are mixed and melt blended and at least one compatibilizer is added at a later time to the melt blend and further melt
5 blended;
- v. Thermoplastic aromatic polyester is melted under appropriate conditions in an extruder and at a later time LCP and at least one compatibilizer are added to the
10 thermoplastic aromatic polyester and further melt blended;
- vi. Thermoplastic aromatic polyester and a first compatibilizer are melt blended and at a later time LCP and a second
15 compatibilizer are added to the melt blend and further mixed and melt blended;
- vii. Thermoplastic aromatic polyester and LCP are mixed and melt blended and two compatibilizers are added to the melt
20 blended and further melt blended; and
- viii. Thermoplastic aromatic polyester, LCP and two compatibilizers are mixed and simultaneously melt blended.
- 25 By controlling the order in which the components of the alloys are mixed and melt blended the properties of the alloy are controlled to enable the production of articles of manufacture, e.g., films, which have improved properties over the properties of a similar article of manufacture composed

solely of thermoplastic aromatic polyester or of LCP and thermoplastic aromatic polyester.

In the production of films from the alloys described above, the meld blend is extruded, e.g., through a slot die, a circular, counter-rotating die,
5 or a circular rotating trimodal die.

In alloys containing two compatibilizers, sequential compatibilization according to methods (iii) and (vi) above are preferred preparation methods. It was unexpectedly discovered that these unique methods of combining two or more compatibilizers, provided alloys having improved properties.
10 While not wishing to be bound by theory, it is believed that in this novel process, two compatibilizers interact sequentially to provide the desired compatibilization and in some cases also interact with each other. In the case of thermoplastic aromatic polyester-LCP blends of the present invention, the interaction is between the thermoplastic aromatic polyester
15 and a first compatibilizer, and the LCP interacts with a second compatibilizer. The products of these two interactions, then sequentially react with one another to form an alloy.

The methods of the present invention provide a great deal of flexibility to achieve the desired compatibilization through the wide array of
20 possibilities for the compatibilizers to interact with the major components of the alloy, which is the object of the compatibilization. The methods of the present invention provide an innovative yet efficient way to achieve the desired end results.

In one preferred embodiment of the present invention, Chevron DS™
25 1328/60, an anhydride-grafted ethylene-methyl acrylate copolymer, was melt blended with thermoplastic aromatic polyester and then Polybond™ 3009, and VECTRA™ A-950 were added to the mixture and further melt blended to produce alloys which were extruded to produce films having

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greatly improved mechanical properties. For example, a tensile strength of 14,800 psi was obtained in one film extruded from an alloy made by feeding 5% of the Chevron DS™ 1328/60 in the hopper with the thermoplastic aromatic polyester, and then by feeding 2% Polybond™ 3009 with the LCP VECTRA™ A-950 into the vent feed port.

In another preferred embodiment, Escor® ATX-325, an ethylene-methyl-methacrylic acid terpolymer, was melt blended with thermoplastic aromatic polyester and then Polybond™ 3009 and Vectra™ A950 were added to the mixture and further melt blended. A tensile modulus value of 1.09 million psi was obtained in a film extruded from an alloy made by feeding 5% of Exxon ATX™ 320 in the hopper with the PAT, and then feeding 2% Polybond™ 3009 with the LCP VECTRA™ A-950 into the vent feed port.

Accordingly, it can be seen that films produced from the alloys of the present invention have surprisingly improved properties over films of LCP and PAT blends or of PAT alone.

Conventional extrusion equipment was used to produce the alloys of the present invention and to extrude films from these alloys. Mixing and melt blending of components to form the alloys of the present invention is carried out using conventional single or double screw extruders. It is preferred that the extruder system has not less than 25/1 L/D ratio. Extrusion conditions such as processing temperatures, rotation speed of the screw, feed rate and through put were optimized for the particular alloy by taking into consideration the properties of the polymers being melt blended to form the alloy, including resulting viscosity of the melt blend. Typically, higher shear screw configurations were found to give better dispersions of the LCP and better compatibilization resulting in alloys that could be used to produce films having improved properties. Typical temperatures

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employed for the processing were 525 to 620°F. The rotation rate of the screw was, typically between 50 to 300 rpm.

The alloy components are appropriately conditioned, e.g., dried and then fed to the extruder using conventional methods. For example, the components can be melt blended and extruded to form pellets. The pellets can then be extruded or injection molded to form the desired article of manufacture. Alternatively, the dry components can be blended, fed into the extruder, and extruded, e.g., to a film directly.

The masterblending or masterbatching technique in which typically, a blend of two components is processed into pellets to form the "masterblend" can also be used. The masterblend can be run through an extruder a second time with additional components added in accordance with the teachings of the present invention. This is a convenient method of manufacture, because an inventory of masterblend material can be made and then combined with different components as desired. One advantage to the masterblending process is that small and very controlled amounts of additional components can be added to the masterblend. For example, if the masterbatch has 10% LCP, the masterbatch can be passed through the extruder again with, for example, 10% of the masterbatch and 90% of the other polymers, providing a masterbatch that is 1% in LCP.

Through masterbatching, controlled low concentration of a component in the alloy can be obtained; and additional mixing and shearing through multi-passes in the extruder can be achieved, if desired.

Masterbatching also provides advantages when working with a component having a low melt temperature, such as the compatibilizer Fusabond® A MG-175D which has a melt temperature of about 45°C. It can be added over time at the vent feed with the LCP. However, in one preferred method of the present invention the LCP and low melt

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temperature compatibilizer are masterbatched, thus allowing greater control over the processing of this low melt temperature component which is also present at a low concentration.

5 The present invention will be further illustrated with reference to the following example which is intended to aid in the understanding of the present invention, but which is not to be construed as a limitation thereof.

EXAMPLE

10 The alloy components should be appropriately treated, e.g., dried, before processing as would be readily apparent to the skilled artisan.

The work described in the following example was carried out using a conventional 25 mm or 40 mm co-rotating, non-intermeshing twin screw extruder manufactured by Berstorff Corporation. Mixing and kneading elements for the screw configuration were varied according to conventional wisdom to achieve the desired degree of mixing.

15 Films were extruded from a slot die, approximately 8 inches wide with die gap of approximately 0.010 to 0.020 inches. Also, a counter-rotating die or circular trimordal die (see, U.S. Patents 4,975,312 and 5,288,529) can be used to extrude films comprising one or more alloys of the present invention. Since the degree of uniaxial orientation produced in the extruded film has an impact on the properties, films having similar extrusion conditions were compared in the work discussed below.

A universal testing machine was used for testing the tensile properties based on ASTM standard tests, e.g., ASTM #0882.

25 The LCP used was Vectra™ A-950 from Hoechst-Celanese Corporation. A PCTA copolymer purchased from Eastman Chemicals under the tradename Kodar® or Eastar™ A150 was used in the following work. Also used was a PET homopolymer purchased from Eastman

- 25 -

Chemical under the tradename Kodapak® or Eastapak™ 7352 and a CPET purchased from Shell under the tradename Traytuff™ CPET. The compatibilizers used included: HYTREL™ HTR-6108; Polybond™ 3009; and Fusabond® E-MB-226D; SP 2205™ and 3306™; DS™ 1328/60 and
5 Fusabond® A MG-175D; Lotader™ 2400; Escor® ATX-320, Escor® ATX-325, and; Escor® XV-1104; and Vamac™ G1.

The run conditions and results are shown in Tables I-VII. In the Tables, the thermoplastic aromatic polyesters used are indicated as follows: Kodar® or Eastar™ A150 as "A150," or Kodar® or Eastar™ 9921 as "9921,"
10 or Kodapak® or Eastapak™ 7352 as "7352" and Shell's Traytuff™ CPET as "CPET." The VECTRA™ LCP is indicated as "A950." "Ten Yld St." indicates Tensile Yield Strength; and "Ten. Mod." indicates Tensile Modulus Values. In the Tables, compatibilizers listed are identified as follows: HYTREL™ HTR-6108 as Hytrel 6108; Polybond™ 3009 as
15 "BP3009"; SP 2205™ as "SP2205"; DS™ 1328/60 as "Chev DS"; Lotader™ 2400 as "Lotader 2400"; Escor® ATX-320, ATX-325 and XV1104s "ATX320", "ATX325" and "XV1104" respectively, and Fusabond® E-MB-226D as "Fusabond226".

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TABLE A

LCP, thermoplastic aromatic polyester and at least one compatibilizer are mixed and melt blended to form an alloy.

5

10

RUN #	HOPPER FEED	TEN YLD ST MD(Kpsi)	TEN MOD MD(Kpsi)	OX- BARRIER
6299-7	85.7%A150+9.5%A950 +4.8%ATX320	10.6	800	27.2
6299-9	85.7%A150+9.5%A950 +4.8%ATX325	9.7	810	-
6299-10	85.7%A150+9.5%A950 +4.8%Chevron	9.1	570	25.3
8249-9	95%8006+4%A950 +4%Hytre16108	7.1	209	-

TABLE B

15

LCP, thermoplastic aromatic polyester and a portion of the total compatibilizer to be used are mixed and melt blended, the remainder of the compatibilizer is added at a later time and further melt blended.

20

25

RUN #	HOPPER FEED	VENT FEED	TEN YLD ST MD (Kpsi)	TEN MOD MD (Kpsi)	OX- BAR RIER
6249-3	85.7%A150+ 9.5%A950 +2.4%ATX325	2.4%ATX325	10.0	421	25.5
6249-7	85.7%A150+ 9.5%A950 +2.4%BP3009	2.4%BP3009	12.9	460	26.8
8319-2	91%8006+2% Hytre16108	1%Fusabond226D +7%A950	6.9	320	-
9085-4	86%7352+1% Hytre16108	10%A950+ 2%Fusabond226D	7.19	263	8.4

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TABLE C

LCP, thermoplastic aromatic polyester and a first compatibilizer are mixed and melt blended. A second compatibilizer is added to the melt blend at a later time and further melt blended.

RUN #	HOPPER FEED	VENT FEED	TEN YLD ST MD(Kpsi)	TEN MOD MD(Kpsi)
6249-8	85.7%A150+ 9.5%A950 +2.4%ATX325	2.4%Lotader 2400	7.2	233

TABLE D

LCP and thermoplastic aromatic polyester are mixed and melt blended and at least one compatibilizer is added at a later time to the melt blend and further melt blended.

RUN #	HOPPER FEED	VENT FEED	TEN YLD ST MD(Kpsi)	TEN MOD MD(Kpsi)	OX- BARRIER
6299-14	85.7%A150+ 9.5%A950	7.8% ATX320	9.1	530	26.6

TABLE E

Thermoplastic aromatic polyester is melted under appropriate conditions in an extruder and at a later time LCP and at least one compatibilizer are added to the PET and further melt blended.

RUN #	HOPPER FEED	VENT FEED	TEN YLD ST MD(Kpsi)	TEN MOD MD(Kpsi)
6309-12	85.7%A150	9.7%A950 +4.8%ATX325	7.1	460
8249-4	94%8006	4%A950 +0.75%SP2260	7.16	233

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TABLE F

Thermoplastic aromatic polyester and a first compatibilizer are melt blended and at a later time LCP and a second compatibilizer are added to the melt blend and further mixed and melt blended.

RUN #	HOPPER FEED	VENT FEED	TEN YLD ST MD(Kpsi)	TEN MOD MD(Kpsi)	OX- BARRIER
7019-7	89%A150 +4.7%ATX320	9.3%A950 +2%BP3009	12.7	810	29.6
7069-8	89%A150 +4.7% ChevronDS	9.3%A950 +2%BP3009	11.2	960	25.7
7069-9	89%A150 +4.7%XV11.04	9.3%A950 +2%BP3009	9.6	740	-
7069-10	89%A150 +4.7% Hytrel6108	9.3%A950 +2%BP3009	9.3	850	20.3
7079-1	89%A150 +4.7% ChevronDS	9.3%A950 +2%BP3009	14.8	840	29.8
8259-3	93%8006 +2%Hytrel6108	4%A950 +1% Fusabond 226D	7.73	278	-

TABLE G

Thermoplastic aromatic polyester & LCP are mixed and melt blended and two compatibilizers are added to the melt blended and further melt blended.

RUN #	HOPPER FEED	VENT FEED	TEN YLD ST MD(Kpsi)	TEN MOD MD(Kpsi)	OX- BARRIER
7069-6	85.7%A150 +9.5%A950	2.4%Hytrel6108 +2.4%BP3009	6.2	420	26.3

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TABLE H

Thermoplastic aromatic polyester, LCP and two compatibilizers are mixed and simultaneously melt blended in an extruder and extruded through a slot die.

RUN #	HOPPER FEED	TEN YLD ST MD(Kpsi)	TEN MOD MD(Kpsi)	OX- BARRIER
7169-3	80%A150+10%A950 +7.5%Hytre16108+2.5%BP3009	7.9	370	25.3

TABLE J

Thermoplastic aromatic polyester, LCP and two compatibilizers are mixed and simultaneously melt blended and extruded through a circular, counter-rotating die.

RUN #	HOPPER FEED	TEN YLD ST MD(Kpsi)	TEN MOD MD(Kpsi)
1199-3	83%A150+10%A950+5%ATX320 +2%BP3009	6.2	440
1199-4	81%A150+10%A950+5%SP2205 +4%BP3009	5.9	370
1199-5	81%A150+10%A950+5%SP2205 +4%Hytre16108	7.2	440

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TABLE K

Thermoplastic aromatic polyester and a first compatibilizer are melt blended and, at a later time, LCP and a second compatibilizer are added to the melt and further mixed and melt blended and extruded using a circular rotating trimodal die.

RUN #	HOPPER FEED	VENT FEED	TEN YLD ST MD(Kpsi)	TEN MOD MD(Kpsi)
3249-2	83.6%A150 +4.4%ATX320	10%A950+2%BP3009	9.0	290
3249-5	83.6%A150 +4.4%ChevronDS	10%A950+2%BP3009	6.5	220

TABLE L

Control thermoplastic aromatic polyester

RUN #	HOPPER FEED	TEN YLD ST MD(Kpsi)	TEN MOD MD(Kpsi)	OX- BARRIER
6249-1	100%A150	5.5	162	-
5269-0	100%A150	5.4	190	-
5119-0	100%A150	5.8	169	-
4239-1	100%A150	6.2	176	31.5
6299-1	100%A150	5.2	320	-
7069-1	100%A150	5.3	320	29.9
3189-1	100%A150	6.2	200	-

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TABLE M

Control thermoplastic aromatic polyester & LCP, No Compatibilizer

5	RUN #	HOPPER FEED	TEN YLD	TEN	OX-
			ST	MOD	
			MD(Kpsi)	MD(Kpsi)	BARRIER
	3189-2	90%A150+10%A950	6.9	290	-
	3189-5	90%A150+10%A950	5.5	210	22.7
	3189-9	90%A150+10%A950	5.8	231	-
	6249-2	90%A150+10%A950	7.4	251	-
	7069-2	90%A150+10%A950	6.1	420	24.9
10	7019-5	90%A150+10%A950	6.1	440	-

TABLE N - Masterbatch

15	RUN #	HOPPER FEED	VENT FEED	TEN YLD	TEN	OX-
				ST	MOD	
				MD(Kpsi)	MD(Kpsi	BARR
))	
	8129-1	83%A150 +5%Hytre16108	10%A950 +2%BP3009	8.0	550	20.6
	8129-5	78%A150 +10%Hytre16108	10%A950 +2%BP3009	7.8	230	19.6
	8129-10	83%A150 +5%Hytre16108	10%A950 +2%BP3009	5.6	430	22.1
	8129-16	78%A150 +10%Hytre16108	10%A950 +2%Hytre16108	5.9	420	18.5
	8129-17	78%A150 +10%Hytre16108	10%A950 +2%Hytre16108	5.8	430	18.4
20	8129-18	78%A150 +10%Hytre16108	10%A950 +2%BP3009	7.4	600	19.5
	8129-19	78%A150 +10%Hytre16108	10%A950 +2%BP3009	7.6	710	18.0
	8289-5	94%7352 +2%Hytre16108	1%A950 +3%Fusabond 226D	7.37	268	

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TABLE O

In some runs, LCP, thermoplastic aromatic polyester and one compatibilizer are added to the hopper feed and melt blended to form an alloy. In other runs, thermoplastic aromatic polyester and one compatibilizer are added to the hopper feed and LCP and Fusabond 226 are added at the vent feed and melt blended to form an alloy.

RUN #	HOPPER FEED	VENT FEED	TEN YLD ST MD (Kpsi)	TEN MOD MD(Kpsi)
9259-1	100%A150	-	5.5	180
9259-2	90%A150+10%A950	-	7.3	560
9259-3	85%A150+10%A950 +5%ATX325	-	8.7	740
9269-1	100%7352	-	5.8	250
9269-2	90%7352+10%A950	-	6.2	290
9269-3	85%7352+10%A950 +5%ATX325	-	7.0	290
9269-4	88%7352+10%A950 +2%Escor325	-	6.7	300
9269-5	86%7352+10%A950 +4%Escor325	-	7.3	300
9269-6	86%7352 +2%Escor325	10%A950 +2%Fusabond226	7.3	320
9269-7	84%7352 +4%Escor325	10%A950 +2%Fusabond226	7.2	310
9269-8	86%7352 +2%Hytrel6108	10%A950 +2%Fusabond226	7.2	310
9269-9	84%7352 +4%Hytrel6108	10%A950 +2%Fusabond226	6.5	260
9269-10A	85%7352 +4%Hytrel6108	10%A950 +1%Fusabond226	6.7	280

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TABLE O - cont'd

5	RUN #	HOPPER FEED	VENT FEED	TEN YLD	TEN
				ST MD	MOD
				(Kpsi)	MD(Kpsi)
10	9269-10B	85%7352 +4%Hytre16108	10%A950 +1%Fusabond226	7.0	340
	9269-11	82%7352 +5%Hytre16108	10%A950 +3%Fusabond226	7.0	320
	9269-12	86%7352 + 10%A950 +4%Hytre16108	-	6.4	310
	9269-13	87%7352 + 10%A950 +3%Hytre16108	-	7.3	340
	9269-14	88%7352 + 10%A950 +2%Hytre16108	-	6.9	330
	9269-15	89%7352 + 10%A950 +1%Hytre16108	-	7.3	320

TABLE P

15

LCP, thermoplastic aromatic polyester and compatibilizer are added to the hopper feed and melt blended to form an alloy.

20

25	RUN #	HOPPER FEED	TEN YLD	TEN MOD
			ST MD	MD (Kpsi)
			(Kpsi)	
	04059-1	90%CPET + 10%950	10	610
	04059-2	86½ %CPET + 10%A950 + 3½ %ATX320	11	640
	04059-3	85%CPET + 10%A950 + 5%ATX320	11.7	620

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TABLE Q

5

LCP, thermoplastic aromatic polyester and compatibilizer are added to the hopper feed and melt blended to form an alloy

10

RUN #	HOPPER FEED	OXYGEN- PERMEABILITY cc-mil/100in ² -day-atm
11169-1	100%7352	28
9269-3	85%7352+5%ATX325+10%A950	9
9269-4	88%7352+2%ATX325+10%A950	9
9269-5	86%7352+4%ATX325+10%A950	9
15 9269-12	86%7352+4%Hytrel6108+10%A950	21
9269-13	87%7352+3%Hytrel6108+10%A950	8
9269-14	88%7352+2%Hytrel6108+10%A950	20
9269-15	89%7352+1%Hytrel+10%A950	22

20

The present invention has been described in detail including the preferred embodiments thereof. However, it would be appreciated that those skilled in the art, upon consideration of the present disclosure, may make modifications and/or improvements on this invention and still be within the scope and spirit of this invention as set forth in the following claims.

25

What is claimed is:

1. An alloy comprising at least one thermotropic liquid crystalline polymer (LCP), at least one thermoplastic aromatic polyester and at least one compatibilizer, wherein the compatibilizer comprises:
 - (i) a copolyester elastomer;
 - (ii) an ethylene ester copolymer;
 - (iii) a copolymer of ethylene and a carboxylic acid or acid derivative;
 - (iv) ethylene ester copolymers grafted with at least one functional monomer;
 - (v) an ethylene copolymer-acrylic acid terpolymer;
 - (vi) terpolymers of ethylene, unsaturated ester and a carboxylic acid or acid derivative; and
 - (vii) an acrylic elastomer.
2. An alloy in accordance with claim 1 wherein:
 - (i) the copolyester elastomer comprises HYTREL™ HTR-6108.
 - (ii) the ethylene ester copolymer comprises an ethylene-methyl acrylate copolymer;
 - (iii) the copolymer of ethylene and a carboxylic acid or acid derivative comprises an ethylene-maleic anhydride copolymer;
 - (iv) the ethylene ester copolymer comprises an ethylene-methyl acrylate copolymer grafted with maleic anhydride;
 - (v) the ethylene copolymer-acrylic acid terpolymer comprises an ethylene-methyl acrylate-maleic anhydride terpolymer;
 - (vi) the terpolymer of ethylene, unsaturated ester and a carboxylic acid or acid derivative comprises an ethylene-methyl acrylate-methacrylic acid terpolymer; and
 - (vii) the acrylic elastomer comprises an acrylic rubber.

3. An alloy in accordance with claim 2 wherein:
 - (i) the ethylene-methyl acrylate copolymer comprises SP 2205™ or 3306™;
 - (ii) the ethylene-maleic anhydride copolymer comprises Polybond™ 3009 or Fusabond® E-MB-226D;
 - (iii) the ethylene-methyl acrylate copolymer grafted with maleic anhydride comprises DS™ 1328/60 or Fusabond® A MG-175D;
 - (iv) the ethylene-methyl acrylate-maleic anhydride terpolymer comprises Lotader™ 2400, Lotader™ 3410, and Lotader™ 5500 from Elf Atochem;
 - (v) the ethylene-methyl acrylate-methacrylic acid terpolymer comprises Escor® ATX-320, Escor® ATX-325 or Escor® XV-1104; and
 - (vi) the acrylic rubber comprises Vamac™ G1
4. An alloy in accordance with claim 1, wherein the copolyester elastomer comprises HYTREL™ HTR-6108.
5. An alloy in accordance with claim 1, wherein the thermotropic LCP comprises a wholly aromatic polyester or copolyester.
6. An alloy in accordance with claim 1, wherein the thermotropic LCP comprises a partially aromatic polyester or copolyester.
7. An alloy in accordance with claim 5, wherein the wholly aromatic polyester or copolyester comprises 6-oxy-2-naphthoyl and p-oxybenzoyl moieties.
8. An alloy in accordance with claim 7, wherein the wholly aromatic polyester or copolyester comprises Vectra™ A-950.
9. An alloy in accordance with claim 5, wherein the wholly aromatic polyester or copolyester comprises hydroxy benzoic acid/phenyl hydroquinone/dimethyl-naphthylene dicarboxylate units.

10. An alloy in accordance with claim 9, wherein the wholly aromatic polyester or copolyester comprises ZENITE™.
11. An alloy in accordance with claim 5, wherein the wholly aromatic polyester or copolyester is XYDAR™, VECTRA™, SUMIKASUPER®, EKONAL™, HX™, ZENITE™, RODRUN® or GRANLAR™.
12. An alloy in accordance with claim 5, wherein the compatibilizer comprises a copolymer elastomer.
13. An alloy in accordance with claim 12, wherein the copolymer elastomer comprises HYTREL™ HTR-6108.
14. An alloy in accordance with claim 13, wherein the thermoplastic polyester is PCTA or a PET homopolymer.
15. An alloy in accordance with claim 14, wherein the PCTA is Kodapak® or Estapak™ A150 and the PET homopolymer is Kodapak® or Estapak™ 7352.
16. An alloy in accordance with claim 5, wherein the barrier properties of the alloy are from 1 to 3 times better than the barrier properties of the thermoplastic aromatic polyester.
17. An alloy in accordance with claims 1 or 2, wherein at least two compatibilizers are present.
18. An alloy in accordance with claim 17, wherein the LCP comprises a wholly aromatic copolyester and the compatibilizers comprise an ethylene-methyl acrylate-acrylic acid terpolymer and an ethylene-maleic anhydride copolymer.

19. An alloy in accordance with claim 18, wherein the ethylene-methyl acrylate-acrylic acid terpolymer comprises Escor™ ATX-320, Escor™ ATX-325, or Escor™ XV-1104 and the ethylene-maleic anhydride comprises Polybond™ 3009 or Fusabond® E-MB-226D.
20. An alloy in accordance with claim 19, wherein the thermoplastic aromatic polyester comprises a PCTA copolymer.
21. An alloy in accordance with claim 20, wherein the PCTA copolymer comprises Kodar® or Eastar® A150.
22. An alloy in accordance with claim 17, wherein the LCP comprises a wholly aromatic copolyester and the compatibilizers comprise an ethylene-methyl acrylate copolymer grafted with maleic anhydride and an ethylene-maleic anhydride copolymer.
23. An alloy in accordance with claim 22, wherein the ethylene-methyl acrylate copolymer grafted with maleic anhydride comprises DS™ 1328/60 or Fusabond® A MG-175D and the ethylene-maleic anhydride copolymer comprises Polybond™ 3009 or Fusabond® E-MB-226D.
24. An alloy in accordance with claim 17, wherein the LCP comprises a wholly aromatic copolyester and the compatibilizers comprise a copolyester elastomer and an ethylene-maleic anhydride copolymer.
25. An alloy in accordance with claim 24, wherein the copolyester elastomer comprises HYTREL™ HTR-6108 and the ethylene-maleic anhydride copolymer comprises Polybond™ 3009 or Fusabond® E-MB-226D.
26. An alloy in accordance with claim 17, wherein the LCP copolyester comprises 6-oxy-2-naphthoyl and p-oxybenzoyl moieties and the compatibilizers comprise an ethylene-

methyl acrylate copolymer grafted with maleic anhydride and an ethylene-maleic anhydride copolymer.

27. An alloy in accordance with claim 26, wherein the copolyester comprises Vectra™ A-950 and the ethylene-methyl acrylate copolymer grafted with maleic anhydride comprises DS™ 1328/60 or Fusabond® A MG-175D and the ethylene-maleic anhydride copolymer comprises Polybond™ 3009 or Fusabond® E-MB-226D.

28. An alloy in accordance with claim 17, wherein the LCP wholly aromatic copolyester comprises 6-oxy-2-naphthoyl and p-oxybenzoyl moieties and the compatibilizers comprise a copolyester elastomer and an ethylene-maleic anhydride copolymer.

29. An alloy in accordance with claim 28, wherein the LCP wholly aromatic copolyester comprises Vectra A-950 and the copolyester elastomer comprises HYTREL™ HTR 6108 and the ethylene-maleic anhydride copolymer comprises Polybond™ 3009 or Fusabond® E-MB-226D.

30. An alloy in accordance with claim 17, wherein the LCP wholly aromatic copolyester comprises 6-oxy-2-naphthoyl and p-oxybenzoyl moieties and the compatibilizers comprise an ethylene-methyl acrylate-acrylic acid terpolymer and an ethylene-maleic anhydride copolymer.

31. An alloy in accordance with claim 28, wherein the LCP wholly aromatic copolyester comprises Vectra A-950 and the ethylene-methyl acrylate-acrylic acid terpolymer comprises Escor™ ATX-320, Escor™ ATX-325, Escor™ XV-1104, or HYTREL™ HTR 6108 and the ethylene-maleic anhydride copolymer comprises Polybond™ 3009 or Fusabond® E-MB-226D.

32. An alloy in accordance with claim 5, wherein the thermoplastic aromatic polyester is a PET homopolymer or copolymer, PBT, PETG, PCTA copolymers, APET, CPET, PCPT or PBN.
33. An alloy in accordance with claim 17, wherein the thermoplastic aromatic polyester is a PET homopolymer or copolymer, PBT, PETG, PCTA copolymers, APET, CPET, PCPT or PBN.
34. An alloy in accordance with claim 32, wherein the PET homopolymer is Kodapak® or Estapak™ A150, the PCTA copolymer is Kodapak® or Estapak™ 7352, and the CPET is Traytuff™.
35. An alloy in accordance with claim 33, wherein the PET homopolymer is Kodapak® or Estapak™ A150, the PCTA copolymer is Kodapak® or Estapak™ 7352, and the CPET is Traytuff™.
35. An alloy in accordance with claim 17, wherein the wholly aromatic polyester of copolyester is XYDAR™, VECTRA™, SUMIKASUPER®, EKONAL™, HX™, ZENITE™,
36. An alloy in accordance with claim 5, wherein the wholly aromatic LCP is Vectra™ A950 and the compatibilizer is Escor ATX325 or HYTREL.
37. A method of producing an alloy comprising at least one thermotropic LCP, PET and at least one compatibilizer, wherein the method comprises melt blending the LCP, PET and compatibilizer to form an alloy.
38. A method in accordance with claim 36, wherein the method comprises melt blending LCP, PET and a portion of a compatibilizer to form a first melt blend, and adding the remainder of the compatibilizer to the first melt blend and further melt blending to form an alloy.

39. A method of producing an alloy comprising at least one thermotropic LCP, PET and a first and second compatibilizer, wherein the method comprises melt blending PET and the first compatibilizer to form a first melt blend, adding LCP and second compatibilizer to the first melt blend, and further melt blending to form an alloy.
40. A method in accordance with claim 39, wherein the method comprises melt blending LCP, PET and the first compatibilizer to form a melt blend, adding the second compatibilizer to the melt blend, and further melt blending to form an alloy.
41. An article of manufacture comprising an alloy according to claims 1 or 2.
42. An article of manufacture according to claim 41, wherein the article comprises a film, a sheet, a tube, or a container.
43. An article of manufacture according to claim 41, wherein the article is provided with a coating comprising glass, metal or polymer.
44. An alloy in accordance with claim 17, wherein the barrier properties of the alloy are from 1 to 3 times better than the barrier properties of the thermoplastic aromatic polyester.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/17114

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C08L 67/02; C08F 20/00

US CL : 525/64, 165, 166, 444, 445

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 525/64, 165, 166, 444, 445

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

World Patents Index (Database WPI)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DATABASE WPIL on Questel, week 9350, London: Derwent Publications, Ltd., AN 93-405771/50, Class A17, WO 93/24574 A (NESTE OY), 09 December 1993, see the entire abstract.	1-44
Y	DATABASE WPIL on Questel, week 9021, London: Derwent Publications, Ltd., AN 90-157827/21, Class A23, EP 369734 A (AMOCO CORPORATION) 23 May 1990, see the entire abstract.	1-44
Y	US, A, 4,172,859 (EPSTEIN) 30 October 1979, see column 5, line 36 to column 6, line 26.	1-44



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

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26 APR 1996

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